AMENDMENTS TO THE SPECIFICATION

Please add the following paragraphs at page 23, beginning after Scheme XXII and before the first listed paragraph:

Example 5

Experimental Procedures for Selected Compounds in Examples 1-4

Preparation of 21. (R)-3-Hydroxy-3-methyl-2-oxo-5-heptenoicacidethylester 2.1323 g (15.00 mmol) 2-diazomethylacetoacetate are dissolved in 75 ml benzene (1 neck 100 ml flask). Under stirring 1.0816 g (15 mmol; 1.3 ml) (S)-(+)-butenol are added to the solution. After addition of 66.3 mg (0.15 mmol; 0.01 eq.) $Rh_2(OAc)_4$ the flask is immersed into a preheated (100-110 °C) oil bath. The mixture is heated under reflux for 30 minutes. After 1 minute vigouros nitrogen evolution starts and lasts for about 2 minutes. After cooling the mixture the solvent is evaporated and the residue is

flashed on silica (4.5 x 15 cm) using hexane/ethylacetate (20%). 1.66 g (59%) of the product are obtained. This relatively low yield (compared to the 74% obtained in the racemic series) must be due to same impurity (water?) in the butenol. b.p. 65-67°/0.35 mm Hg; IR (thin film/NaCl) 3521.0 (m), 3028.5 (w), 2981.5 (m), 2957.1 (m), 2937.9 (m), 2919.9 (m), 2857.4 (w), 1742.6 (s), 1726.1 (s), 1452.3 (m), 1437.5 (m), 1376.0 (w), 1361.2 (w), 1289.1 (m), 1250.1 (m), 1192.6 (w), 1145.8 (w), 1116.3 (w), 1081.5 (w), 1060.1 (w), 1032.1 (s), 971.9 (m), 920.3 (w), 861.6 (w), 844.7 (w), 814.4 (w), 722.7 (w), 663.1 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.57 (m, 1H), 5.35 (m, 1H), 3.88 (s, 3H), 3.28 (br.s, 1H), 2.68 (dd, J=7.0, 14.0 Hz, 1H), 2.42 (dd, J=7.7, 14.0 Hz, 1H), 1.66 (d, J=6.42 Hz, 3H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.58, 162.78, 130.97, 123.58, 78.30, 52.55, 42.26, 24.15, 17.82; HRMS (CI, isobutane) *m/z* calc'd for $C_9H_{15}O_4$ (M+H): 187.0970, found 187.0966; $[\alpha]_D^{22}$ + 14.65° (c=1.08, $CHCl_3$).

Preparation of 22. (S)-2-Hydroxy-2-allylmethylmethylacetoacetate 3.35 g (18 mmol) (R)-3-hydroxy-3-methyl-2-oxo-5-heptenoicacidethyl-ester are dissoved in 180 ml dichloromethane and treated with 2.554 g (18 mmol; 2.21 ml) $BF_3 \cdot OEt_2$. The reaction mixture is stirred 2 hours at 25 °C (TLC control). The solvent is evaporated and the residue flashed on silica (4.5 x 18 cm) using hexane/ethylacetate (20%). 2.368 g (71%) of the product are isolated. IR (thin film/NaCl) 3476.1 (m), 3031.2 (w), 3009.6 (w), 2956.2 (m), 2921.4 (w), 2857.5 (w), 1746.9 (s), 1721.9 (s), 1437.4 (m), 1357.9 (m), 1271.0 (m), 1224.2 (m), 1195.9 (m), 1183.2 (m), 1141.0 (m), 1108.5 (m), 1076.9 (w), 1052.8 (w), 994.6 (w), 972.4 (m), 861.8 (w), 816.7 (w), 798.3 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (m, 1H), 5.32 (m, 1H), 4.17 (s, 1H), 3.80 (s, 3H), 2.77 (dd, J=6.6, 14.3 Hz, 1H), 2.63 (dd, J=7.6, 14.3 Hz, 1H), 2.28 (s, 3H), 1.65 (d, J=6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.28, 170.85, 130.59, 122.91, 83.89, 53.16, 38.54, 24.76, 17.94; HRMS (CI, isobutane) *m/z* calc'd for $C_9H_{15}O_4$ (M+H): 187.0970, found 187.0969; $[\alpha]_D^{22}$ - 32.13° (c=1.08, $CHCl_3$). (S)-2-Hydroxy-2-allylmethylmethylacetoacetate (1 pot procedure) 426.5 mg (3.00 mmol) 2-diazomethylacetoacetate are dissolved in 15 ml benzene (1 neck 25 ml flask). Under stirring 237.9 mg (3.3 mmol; 0.286 ml; 1.1 eq.) (S)-(+)-butenol are added to the solution. After addition of 13.3 mg (0.03 mmol; 0.01 eq.) $Rh_2(OAc)_4$ the flask is immersed into a preheated (100-110 °C) oil bath. The mixture is heated under reflux for 80 minutes. After 1 minute vigouros

nitrogen evolution starts and lasts for about 2 minutes. After cooling the reaction mixture 554.5 mg (3.75 mmol; 0.46 ml; 1.25 eq.) $BF_3 \cdot OEt_2$ are added. The mixture is stirred for 2-3 hours (TLC control) at 25 °C. The reaction mixture is passed through silica (2.5 x 8 cm) using pentane/ether (20%) as solvent; 416.9 mg (75%) of the product are isolated.

Preparation of 27. (S)-(+)-Hydroxy furanose and (S)-(-)-methylketonedimethylacetal 1.305 g (7.00 mmol) (S)-2-hydroxy-2-allylmethylmethylacetoacetate and a trace of sudan red dye are dissolved in 45 ml methanol. After cooling to -78 °C the mixture is treated with O_3 until the dye is completely discolored (about 3 minutes). The mixture is purged with argon for 10 Minutes at -78 °C and 20 ml dimethylsulfide are added at that temperature. The dry ice cold bath is replaced with an ice bath which is allowed to thaw (0-20 °C) over a period of 3 hours. The solvent is removed and the crude product dissoved in in 45 ml benzene. After addition of 20.0 mg (0.105 mmol; 0.015 eq.) p-toluenesulfonic acid and 12 ml methanol the mixture is stirred at 25 °C for 17 hours (until the reaction is completed as judged by TLC). The solvent is evaporated and the product is flashed on silica (4.5 x 20 cm) using hexane/ethylacetate (20%) as solvent system. 1.69 g (80%) of a mixture (1:1:1) of two furanose diastereomers and the methylketonedimethylacetal is obtained. They can be separated using HPLC. In a first run (stationary phase: SiO_2; mobile phase: hexane/dichloromethane/ethylacetate (2:2:1) a mixture of the furanose diastereomer I and the metyhylketone is eluated first followed by the second furanose diastereomer which can be isolated in its pure form. The two component mixture is separated using a different system (stationary phase: SiO_2; mobile phase: hexane/*i*-propanol (10%)). The furanose diastereomer I is eluated as first fraction closely followed by the methylketonedimethyl acetal. Hydroxyfuranose mp 81-82 °C; IR (thin film/NaCl) 3495.1 (m), 2995.3 (m), 2953.2 (s), 2917.2 (s), 2848.3 (m), 1747.11 (s), 1463.77 (m), 1439.35 (m), 1379.1 (m), 1355.2 (w), 1263.5 (s), 1200.0 (s), 1182.1 (m), 1156.1 (m), 1121.86 (s), 1086.1 (s), 1043.7 (m), 1019.3 (m), 973.677 (m), 949.3 (m), 929.7 (m), 892.27 (m), 864.6 (w), 833.7 (m), 802.7 (m), 750.6 (m), 685.5 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.07 (dd, J=0.6, 5.8 Hz, 1H), 3.79 (s, 3H), 3.42 (s, 3H), 3.38 (br. s, 1H), 3.25 (s, 3H), 3.03 (dd, J=5.8, 14.2 Hz, 1H), 2.06 (d, J=14.2 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.50, 110.55, 103.86, 83.17, 55.56, 52.63,

49.28, 40.56, 15.82; $[\alpha]_D^{20}$ + 112.18° (c=1.06, $CHCl_3$). Methylketone IR (thin film/NaCl) 3450.0 (m), 2988.3 (m), 2953.5 (s), 2915.0 (s), 2849.2 (s), 1746 (s), 1722.3 (s), 1457.5 (m), 1436.4 (m), 1386.7 (m), 1275.0 (m), 1245.2 (m), 1198.0 (m), 1178.1 (m), 1142.1 (s), 1121.0 (s), 1063.3 (s), 1014.2 (w), 998.1 (w), 974.4 (w), 907.4 (w), 830.6 (w), 755.1 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.50 (s, 1H), 4.50 (dd, J=4.8, 6.7 Hz, 1H), 3.78 (s, 3H), 3.34 (s, 3H), 3.29 (s, 3H), 2.43 (dd, J=4.8, 14.5 Hz, 1H), 2.39 (dd, J=6.7, 14.5 Hz, 1H), 2.28 (s, 3H); ^{18}C NMR (125 MHz, $CDCl_3$) δ 204.04, 170.87, 102.01, 81.80, 54.99, 53.84, 53.22, 38.40, 24.50; $[\alpha]_D^{20}$ - 20.25° (c=0.97, $CHCl_3$). Hydroxyfuranose mp 63-64 °C; IR (thin film/NaCl) 3480.7 (m), 2995.0 (w), 2953.3 (m), 2914.2 (w), 2835.1 (w), 1726.7 (s), 1443.2 (m), 1377.9 (m), 1348.2 (w), 1278.2 (s), 1239.0 (m), 1228.0 (m), 1200.4 (m), 1181.6 (w), 1165.1 (s), 1127.6 (s), 1114.3 (s), 1092.2 (m), 1084.5 (m), 979.6 (m), 957.5 (m), 948.7 (m), 927.8 (m), 901.5 (m), 871.9 (w), 840.9 (w), 802.9 (w), 755.5 (m), 673.0 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.21 (app. t, J=5.7 Hz, 3H), 3.79 (s, 3H), 3.47 (s, 3H), 3.36 (d, J=1.6 Hz, 1H), 3.27 (s, 3H), 2.84 (ddd, J=1.6, 5.2, 14.3 Hz, 1H), 2.34 (dd, J=6.2, 14.3 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.10, 1089.84, 105.38, 84.46, 56.37, 52.82, 49.00, 40.44, 14.46; HRMS (CI, isobutane) *m/z* calc'd for $C_8H_{13}O_5$ (M-CH_3OH+H): 189.0763, found 189.0764; $[\alpha]_D^{22}$ + 9.66° (c=1.03, $CHCl_3$).

Preparation of 38. (R)-2-Hydroxy-2-allylhexylmethylacetoacetate 426.5 mg (3.00 mmol) 2-diazomethylacetoacetate are dissolved in 15 ml benzene (1 neck 25 ml flask). Under stirring 469.3 mg (3.3 mmol; 1.1 eq.) (R)-(-)-nonenol are added to the solution. After addition of 13.3 mg (0.03 mmol; 0.01 eq.) $Rh_2(OAc)_4$ the flask is immersed into a preheated (100-110 °C) oil bath. The mixture is heated under reflux for 30 minutes. After 1 minute vigouros nitrogen evolution starts and lasts for about 2 minutes. After cooling the reaction mixture 554.5 mg (3.75 mmol; 0.46 ml; 1.25 eq.) $BF_3 \cdot OEt_2$ are added. The mixture is stirred for 2-3 hours (TLC control) at 25 °C. The reaction mixture is passed through silica (2.5 x 8 cm) using pentane/ether (20%) as solvent; 510.9 mg (66%) of the product are isolated. R)-(-)-Hydroxy furanose and (R)-(+)-methylketonedimethylacetal The same procedure that was employed for the preparation of (S)-(+)-hydroxy furanose and (S)-(-)-methylketonedimethylacetal is used. 1.798 g (7.00 mmol) of (R)-2-hydroxy-2-allylhexylmethylacetoacetate are used as

starting material yielding 1.04 g (68%) of the 3 component mixture (1:1:1). Hydroxyfuranose mp 81-82 °C; IR (thin film/NaCl) 3496.4 (m), 2998.9 (m), 2953.3 (m), 2915.1 (m), 2836.9 (m), 1748.9 (s), 1732.9 (s), 1440.3 (m), 1379.3 (m), 1334.7 (w), 1261.7 (s), 1200.7 (s), 1182.7 (m), 1156.9 (s), 1122.5 (s), 1098.5 (s), 1086.5 (s), 1044.3 (m), 1021.1 (m), 975.9s, 94826 (m), 930.7 (m), 893.9 (m), 865.4 (m), 834.9 (m), 802.2 (m), 750.9 (m), 685.7 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.07 (d, J=5.8 Hz, 1H), 3.78 (s, 3H), 3.42 (s, 3H), 3.25 (s, 3H), 3.03 (dd, J=5.8, 14.1 Hz, 1H), 2.05 (d, J=14.1 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.41, 110.46, 103.78, 83.08, 55.47, 52.52, 49.18, 40.49, 15.73; $[\alpha]_D^{20}$ - 122.55° (c=1.10, $CHCl_3$). Methylketone IR (thin film/NaCl) 3452.5 (m), 2993.2 (m), 2954.6 (m), 2934.2 (m), 2917.5 (m), 2848.4 (m), 2838.2 (m), 1748.7 (s), 1723.1 (s), 1437.8 (m), 1359.7 (m), 1275.8 (m), 1245.7 (m), 1198.5 (m), 1178.2 (m), 1144.7 (s), 1124.4 (s), 4065.4 (s), 1015.7 (m), 997.3 (m), 905.2 (m), 829.6 (w), 802.0 (w), 756.0 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.51 (br. s, 1H), 4.50 (dd, J=4.9, 6.6 Hz, 1H), 3.78 (s, 3H), 3.34 (s, 3H), 3.29 (s, 3H), 2.43 (dd, J=4.9, 14.6 Hz, 1H), 2.38 (dd, J=6.6, 14.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.00, 170.84, 101.96, 81.76, 54.92, 53.79, 53.18, 38.37, 24.46; $[\alpha]_D^{20}$ + 19.55° (c=1.12, $CHCl_3$). Hydroxyfuranose mp 63-64 °C; IR (thin film/NaCl) 3486.7 (m), 2994.8 (m), 2954.8 (m), 2918.0 (m), 2836.2 (m), 1732.7 (s), 1442.6 (m), 1378.3 (m), 1346.6 (w), 1276.5 (s), 1243.0 (m), 1229.7 (m), 1199.7 (m), 1183.0 (m), 1165.4 (s), 1126.7 (s), 1115.6 (s), 1086.6 (s), 1049.2 (s), 1020.2 (s), 980.1 (m), 956.6 (m), 626.1 (m), 902.6 (m), 870.2 (w), 840.2 (w), 803.0 (w), 754.6 (m), 673.3 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.21 (app. t, J=5.7 Hz, 1H), 3.79 (s, 3H), 3.47 (s, 3H), 3.36 (br. s, 1H), 3.27 (s, 3H), 2.84 (dd, J=5.3, 14.3 Hz, 1H), 2.34 (dd, J=6.2, 14.3 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.11, 109.86, 105.40, 84.48, 56.39, 52.83, 49.02, 40.46, 14.48; $[\alpha]_D^{20}$ -9.00° (c=1.16, $CHCl_3$).

General method for the preparation of 30a-d Dry N_2 is bubbled through a mixture of 2,2'-biindole (0.86 mmol), diazo compound 4 (2.2 mmol, 2.5 eq), $Rh_2(OAc)_4$ (0.086 mmol, 0.1 eq) and 8.6 mL pinacolone, in a 3-neck round bottom flask fitted with a reflux condenser for 2 h. The reaction mixture is then heated to reflux for 8 h. The mixture is allowed to cool to 25 °C, the solvent is evaporated, the residue is chromatographed (1:1 EtOAc:Hexanes) to provide (R= 3,4-DMB 0.25 g, 0.56 mmol, 65%; R=4-

PMB 0.22 g, 0.47 mmol, 55%; R=Bn 0.20 g, 0.5 mmol, 58%; R=*t*-Bu 0.13 g, 0.34 mmol, 40%).

Indolocarbazole **30a**. IR (thin film/NaCl) 3485.3 (brm), 3456.0 (brm), 3343.1 (brs), 3249.7 (brm), 2979.7 (m), 1654.4 (w), 1600.5 (s), 1578.2 (s), 1465.8 (w), 1446.5 (m), 1385.0 (s), 1364.0 (m), 1335.9 (w), 1225.3 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ 11.45 (bs, 1H), 11.29 (bs, 1H), 9.24 (d, *J*=7.9 Hz, 1H), 8.09 (d, *J*=7.8 Hz, 1H), 7.77 (d, *J*=8.2 Hz, 1H), 7.70 (d, *J*=8.2 Hz, 1H), 7.47 (app.t, *J*=7.5 Hz, 1H), 7.41 (app.t, *J*=7.5 Hz, 1H), 7.30 (app.t, *J*=7.5 Hz, 1H), 7.21 (app.t, *J*=7.5 Hz, 1H), 5.13 (s, 2H), 1.65 (s, 9H); ^{13}C NMR (62.5 MHz, DMSO-d6) δ 169.9, 139.2, 139.0, 129.9, 127.6, 125.4, 125.3, 124.9, 122.7, 122.4, 122.0, 121.2, 119.7, 118.8, 115.1, 113.6, 111.8, 111.2, 101.9, 53.6, 48.1, 27.8; HRMS (FAB) *m/z* calc'd for $C_{24}H_{22}N_3O$ (M+H): 368.1762, found 368.1764.

Indolocarbazole **30b**. IR (thin film/NaCl) 3487.5 (brs), 3352.0 (brs), 3232.0 (brs), 3022.3 (m), 1579.1 (s), 1571.2 (s), 1517.7 (s), 1462.9 (s), 1399.3 (m), 1262.7 (m), 1237.6 (s), 1142.0 (w), 1016.8 (w), 741.3 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ 11.50 (bs, 1H), 11.35 (bs, 1H), 9.28 (d, *J*=7.9 Hz, 1H), 7.97 (d, *J*=7.8 Hz, 1H), 7.77 (d, *J*=8.1 Hz, 1H), 7.73 (d, *J*=8.1 Hz, 1H), 7.45 (app.t, *J*=6.9 Hz, 1H), 7.44 (app.t, *J*=7.1 Hz, 1H), 7.26 (app.t, *J*=7.1 Hz, 1H), 7.25 (app.t, *J*=7.1 Hz, 1H), 7.02 (s, 1H), 6.92 (s, 2H), 4.94 (s, 2H), 4.82 (s, 2H), 3.74 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d6) δ 169.2, 148.9, 148.1, 139.1, 139.0, 130.6, 130.0, 127.7, 125.3, 124.9, 124.9, 124.8, 122.6, 122.3, 120.7, 119.9, 119.7, 118.8, 118.2, 115.4, 113.8, 112.3, 112.1, 111.7, 111.1, 55.5, 49.3, 45.4; HRMS (FAB) *m/z* calc'd for $C_{29}H_{24}N_3O_3$ (M+H): 462.1817, found 462.1813.

Indolocarbazole **30c**. IR (thin film/NaCl) 3429.3 (brs), 3351.3 (brs), 2912.4 (m), 1609.7 (s), 1580.3 (s), 1512.0 (s), 1465.5 (s), 1402.1 (w), 1250.61 (s), 1238.4 (s), 1177.3 (m), 1030.8 (w), 748.9 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ 11.53 (bs, 1H), 11.37 (bs, 1H), 9.28 (d, *J*=7.8 Hz, 1H), 7.99 (d, *J*=7.7 Hz, 1H), 7.78 (d, *J*=8.1 Hz, 1H), 7.75 (d, *J*=8.1 Hz, 1H), 7.47 (app.t, *J*=7.0 Hz, 1H), 7.45 (app.t, *J*=7.1 Hz, 1H), 7.36 (d, *J*=8.4 Hz, 2H), 7.28 (app.t, *J*=7.9 Hz, 1H), 7.26 (app.t, *J*=7.8 Hz, 1H), 6.94 (d, *J*=8.5 Hz, 2H), 4.94 (s, 2H), 4.83 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d6) δ 169.2, 158.4, 139.1, 139.0, 130.0, 129.9, 128.9, 127.7, 125.3, 124.9, 124.8,

122.6, 122.2, 120.7, 119.7, 118.8, 118.2, 115.4, 113.9, 113.8, 111.7, 111.1, 54.9, 49.2, 45.0; HRMS (FAB) m/z calc'd for $C_{28}H_{22}N_3O_2$ (M+H): 432.1712, found 432.1699.

(+)-N-3,4-Dimethoxybenzyl-K252a (36). Aglycone 30c (0.22 mmol) and (-)-2,5-dimethoxy sugar (0.87 mmol, 4.0 eq) were refluxed in dry 1,2-dichloroethane (7.5 mL) in the presence of camphorsulfonic acid (0.022 mmol, 0.1 eq) for 48 h. The reaction mixture was allowed to cool to 25 °C, diluted with 5.0 mL CH_2Cl_2, and washed with 5.0 mL 10% $NaHCO_3$ sln. The organic layer was evaporated and purified by preparative tlc (1:60, MeOH:70% CH_2Cl_2 / hexanes, 3 elutions) giving (+)-36 (75.0 mg, 0.120 mmol, 55%) and (+)-37 (34.0 mg, 0.055 mmol, 25%).

Indolocarbazole (+)-36. IR (thin film/NaCl) 3279.7 (brm), 3012.1 (m), 2952.1 (m), 2930.1 (m), 2850.1 (w), 1732.2 (m), 1646.2 (s), 1590.4 (m), 1513.7 (s), 1460.2 (s), 1260.3 (s), 1139.5 (s), 1028.1 (m), 744.5 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ 9.26 (d, J=7.9 Hz, 1H), 7.99 (d, J=7.7 Hz, 1H), 7.92 (app.t, J=8.0 Hz, 2H), 7.49 (app.t, J=7.7 Hz, 1H), 7.47 (app.t, J=7.8 Hz, 1H), 7.32 (app.t, J=7.9 Hz, 1H), 7.30 (app.t, J=8.1 Hz, 1H), 7.15 (dd, J=5.2, 6.9 Hz, 1H), 7.02 (s, 1H), 6.94 (d, J=9.0 Hz, 1H), 6.92 (d, J=9.0 Hz, 1H), 6.35 (s, 1H), 5.0 (dd, J=17.8, 25.9 Hz, 2H), 4.84 (dd, J=15.5, 17.5 Hz, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.39 (dd, J=7.3, 14.0 Hz, 1H), 2.13 (s, 3H), 2.00 (dd, J=4.7, 14.0 Hz, 1H); ^{13}C NMR (62.5 MHz, DMSO-d6) δ 172.6, 168.6, 148.9, 148.2, 139.8, 136.7, 130.4, 130.0, 128.2, 125.3, 125.3, 124.8, 123.9, 123.8, 122.4, 120.9, 120.2, 119.8, 119.3, 118.9, 115.6, 114.6, 114.2, 112.3, 112.1, 108.8, 99.3, 84.8, 55.5, 52.4, 49.5, 45.4, 42.4, 22.6; HRMS (FAB) m/z calc'd for $C_{36}H_{32}N_3O_7$ (M+H): 618.2240, found 618.2240; $[\alpha]_D^{20}$ (+)-15° (c=0.1, MeOH).

Indolocarbazole (+)-37. IR (thin film/NaCl) 3462.3 (brm), 3014.0 (m), 2952.3 (m), 2925.1 (m), 2849.7 (m), 1730.8 (s), 1645.0 (m), 1514.7 (m), 1455.6 (s), 1403.9 (m), 1348.5 (m), 1312.6 (m), 1257.2 (s), 1235.0 (s), 1138.1 (s), 1068.8 (m), 1027.3 (m), 750.3 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ 9.54 (d, J=7.9 Hz, 1H), 8.01 (d, J=7.9 Hz, 1H), 7.94 (d, J=8.2 Hz, 1H), 7.89 (d, J=8.5 Hz, 1H), 7.50 (app.t, J=7.5 Hz, 1H), 7.45 (app.t, J=7.5 Hz, 1H), 7.30 (app.t, J=7.5 Hz, 1H), 7.29 (app.t, J=7.6 Hz, 1H), 7.14 (dd, J=5.0, 7.2 Hz, 1H), 7.01 (d, J=0.71 Hz, 1H), 6.92 (app.t, J=8.2 Hz, 1H), 6.92 (dd, J=1.1, 8.4 Hz, 1H), 6.34 (bs, 1H), 4.97 (dd, J=17.9, 21.3 Hz, 2H), 4.83 (dd, J=15.1, 21.9 Hz, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.40

(dd, *J*=7.5, 14.0 Hz, 1H), 2.14 (s, 3H), 2.05 (dd, *J*=4.8, 14.0 Hz, 1H); ^{13}C NMR (62.5 MHz, DMSO-d6) δ 172.6, 168.9, 149.0, 148.2, 139.7, 136.8, 130.4, 126.2, 126.1, 125.4, 125.1, 124.9, 124.3, 122.0, 121.3, 120.2, 119.8, 119.2, 118.7, 116.3, 113.9, 113.8, 112.3, 112.1, 109.4, 99.3, 84.9, 84.8, 55.5, 52.4, 49.0, 45.4, 42.5, 22.8; HRMS (FAB) *m/z* calc'd for $C_{36}H_{32}N_3O_7$ (M+H): 618.2240, found 618.2240; $[\alpha]_D^{20}$ (+)-13° (c=0.1, MeOH).

(+)-K252a (14). To a stirred solution of (+)-36 (17.0 mg, 0.028 mmol) in CH_2Cl_2 (1.4 mL) at 25 °C was added thioanisole (0.16 mL, 1.4 mmol, 50 eq) followed by 2,2,2-trifluoroacetic acid (1.4 mL). The solution was stirred for 6 h, at which point 2.0 mL sat. $NaHCO_3$ sln. was added dropwise to neutralize the reaction mixture, the organic layer was separated, evaporated and purified via preparative tlc (1:40, MeOH:50% CH_2Cl_2 / hexanes, 3 elutions) giving (+)-K252a (10.8 mg, 0.023 mmol, 83%).

Preparation of desamido K252a (40) To a suspension of indolo[2.3-a]carbazole (10) (1.0 g, 3.9 mmol) in 1,2-dichloroethane (130 mL) was added furanose 9 (1.8 g, 8.2 mmol) followed by CSA (100 mg, 0.43 mmol). The suspension was heated at reflux for 48 h, following which the reaction was allowed to cool to room temperature and was diluted with CH_2Cl_2 (100mL), washed with 10% $NaHCO_3$ (aq.), dried over Na_2SO_4 and chromatographed on silica gel using 3:1 hexanes:ethyl acetate as eluent to afford indolocarbazole 40 (1.37 g, 85%) as a yellow foam. ^1H NMR (500 MHz, acetone-d6): δ 8.18 (app.t, J=6.6 Hz, 1H), 8.18 (app.t, J=5.4 Hz, 1H), 8.00 (m, 2H), 7.89 (d, J=8.5 Hz, 1H), 7.75 (d, J=8.2 Hz, 1H), 7.44 (td, J=0.9, 7.6 Hz, 1H), 7.38 (td, J=1.0, 7.9 Hz, 1H), 7.26 (app.t, J=6.9 Hz, 1H), 7.25 (app.t, J=7.1 Hz, 1H), 7.10 (dd, J=4.9, 7.3 Hz, 1H), 5.18 (s, 1H), 3.99 (s, 3H), 3.44 (dd, J=7.5, 14.0 Hz, 1H), 2.21 (s, 3H), 2.19 (dd, J=4.9, 14.0 Hz, 1H). ^{13}C NMR (125 MHz, acetone-d6): δ 174.1, 140.8, 138.1, 127.7, 127.0, 125.6, 125.6, 125.5, 125.4, 121.6, 121.5, 121.2, 120.5, 120.4, 120.3, 115.0, 113.1, 112.8, 109.6, 99.9, 86.1, 86.0, 53.3, 43.2, 28.3. IR (thin film/NaCl): 3501.3 (brm), 3047.5 (m), 3006.7 (m), 2950.6 (m), 1729.4 (s), 1640.2 (m), 1568.1 (m), 1441.1 (s), 1305.9 (s), 1230.3 (s), 1128.1 (s), 740.0 (s) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{25}H_{20}N_2O_4$: 412.1423. Found: 412.1419.

Preparation of aldehyde 41 To a stirred solution of ester 11 (1.0 g, 2.43 mmol) in THF (24.3mL), was added $LiBH_4$ (106 mg, 4.85 mmol) at room

temperature. After 20 min the solvent was removed in vacuo. To the white residue was added 50 mL 1.0 N HCl on an ice bath. The aqueous phase was extracted with CH_2Cl_2 (3x 50mL). The combined organic phases were dried with Na_2SO_4 and chromatographed on silica gel using 1:1 hexanes:ethyl acetate as eluent to afford a diol (815 mg, 87%) as a white solid. ^1H NMR (500 MHz, acetone-d6): δ 8.18 (d, J=7.6 Hz, 1H), 8.15 (d, J=7.8 Hz, 1H), 7.96 (s, 2H), 7.89 (d, J=8.5 Hz, 1H), 7.65 (d, J=8.1 Hz, 1H), 7.42 (app.t, J=7.6 Hz, 1H), 7.36 (app.t, J=8.2 Hz, 1H), 7.25 (app.t, J=7.6 Hz, 1H), 7.23 (app.t, J=7.4 Hz, 1H), 6.91 (dd, J=5.2, 7.4 Hz, 1H), 4.57 (s, 1H), 4.18 (app.t, J=5.9 Hz, 1H), 4.06 (dd, J=5.4, 11.1 Hz, 1H), 3.90 (dd, J=7.1, 11.1 Hz, 1H), 3.30 (dd, J=7.6, 13.8 Hz, 1H), 2.23 (dd, J=5.1, 13.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, acetone-d6): δ 140.2, 137.4, 127.6, 126.3, 125.4, 125.0, 124.6, 124.6, 120.7, 120.6, 119.9, 119.5, 114.6, 112.2, 112.0, 108.8, 100.1, 84.2, 83.8, 65.5, 40.6, 21.5. IR (thin film/NaCl): 3416.8 (brs), 3052.9 (m), 3010.5 (m), 2955.4 (w), 1732.7 (w), 1640.9 (m), 1568.5 (m), 1492.6 (m), 1459.0 (s), 1441.4 (s), 1309.0 (s), 1233.1 (s), 1031.9 (s), 741.0 (s) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{24}H_{20}N_2O_3$: 384.1474. Found: 384.1472. To a stirred solution of the diol (500 mg, 1.3 mmol) in 1:1 benzene:DMSO (8.7 mL) was added pyridinium trifluoroacetate (250 mg, 1.3 mmol) followed by 1,3-dicyclohexylcarbodiimide (810 mg, 3.9 mmol). The flask was then quickly sealed with a septum, evacuated, and flushed with N_2 (3x). The heterogeneous mixture was stirred for 7h until reaction was complete as indicated by TLC. Benzene (15 mL) was added to the mixture and the 1,3-dicyclohexylurea (DCU) precipitate was filtered. The filtrate was washed with H_2O (3x20 mL), and the combined aqueous layers were back extracted with CH_2Cl_2 (3x30mL). All organic layers were combined, dried with Na_2SO_4, and evaporated to an oily residue. A minimum amount of acetone (2 mL) was added to precipitate the remaining DCU. Filtration and evaporation to a yellow oil, which was puified by MPLC (3:1 hexanes:ethyl acetate) gave aldehyde 41 (375 mg, 73%, 63% 2 steps) as a yellow powder. ^1H NMR (500 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.99 (app.t, J=7.3 Hz, 2H), 7.78 (s, 2H), 8.02 (d, J=8.4 Hz, 1H), 7.29 (app.t, J=7.4 Hz, 1H), 7.24 (app.t, J=7.2 Hz, 1H), 7.22 (d, J=8.4 Hz, 1H), 7.17 (app.t, J=7.9 Hz, 1H), 7.15 (app.t, J=7.2 Hz, 1H), 6.59 (dd, J=5.0, 7.4 Hz, 1H), 3.08 (s, 1H), 2.76 (dd, J=7.6, 14.6 Hz, 1H), 1.99 (s, 3H), 1.83 (dd, J=5.0, 14.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 139.3, 136.9, 126.3, 126.3, 125.1, 124.7, 124.1, 121.2, 121.1, 120.8, 120.3, 120.3, 119.9, 113.1,

112.9, 112.2, 108.0, 97.7, 87.7, 84.0, 89.7, 23.0. IR (thin film/NaCl): 3486.7 (brm), 3054.6 (m), 3007.7 (m), 2945.3 (m), 2843.4 (w), 1723.9 (m), 1641.8 (m), 1568.6 (m), 1458.7 (m), 1441.1 (s), 1309.2 (s), 1232.5 (s), 1128.8 (m), 1004.2 (m), 741.7 (s) cm^{-1}.HRMS (EI) *m/z* Calc'd for $C_{24}H_{18}N_2O_3$: 382.1317. Found: 382.1319.

Preparation of hydroxy ketone 43 To a suspension of aldehyde 12 (75 mg, 0.196 mmol) in Et_2O (5.0 mL) was added $BF_3 \cdot OEt_2$ (27 μL, 0.216 mmol) and the mixture stirred vigorously for 6h. CH_2Cl_2 (25 mL) was added to solubilize the suspension and the resulting solution was evaporated onto SiO_2 (100mg) and chromatographed using 2:1 hexanes:ethyl acetate as eluent to provide ketone 43 (47 mg, 60%) as a white powder. ^1H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J=7.7 Hz, 1H), 8.10 (d, J=7.7 Hz, 1H), 7.97 (d, J=8.5 Hz, 1H), 7.92 (d, J=8.2 Hz, 1H), 7.90 (d, J=8.2 Hz, 1H), 7.43 (app.t, J=7.7 Hz, 1H), 7.39 (app.t, J=7.8 Hz, 1H), 7.32 (app.t, J=7.4 Hz, 1H), 7.28 (app.t, J=7.5 Hz, 1H), 7.25 (d, J=8.1 Hz, 1H), 7.06 (d, J=7.3 Hz, 1H), 4.89 (d, J=6.0 Hz, 1H), 3.55 (dd, J=7.5, 14.3 Hz, 1H), 3.49 (d, J=6.5 Hz, 1H), 2.99 (d, J=14.4 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 140.2, 136.3, 126.4, 125.7, 125.4, 125.1, 124.8, 124.6, 121.4, 120.8, 120.4, 120.2, 119.8, 115.2, 112.7, 112.4, 112.1, 107.9, 100.3, 84.03, 81.6, 44.7, 29.5. IR (thin film/NaCl): 3328.6 (brm), 3048.0 (w), 2923.7 (m), 2852.1 (w), 1731.4 (s), 1637.4 (m), 1441.5 (s), 1395.3 (m), 1312.0 (s), 1130.1 (m), 740.8 (s) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{24}H_{18}N_2O_3$: 382.1317. Found: 382.1315.

Preparation of methoxy ketone 44 Montmorillonite Clay K-10 (1.2 g) was premixed with trimethylorthoformate (1.78 mL, 16.3 mmol) and immediately transfer to a stirred solution of aldehyde 12 (414 mg, 1.1 mmol) in $CHCl_3$ (11 mL) aided by an additional 3 mL $CHCl_3$. The reaction was monitored by TLC (3:1 hexanes:ethyl acetate) and after approximately 0.5 h formation of the dimethyl acetal 16 was complete. The reaction mixture was filtered, and the filtrate evaporated *in vacuo*. The residue was dissolved in diethyl ether (110 mL) under an inert atmosphere, followed by addition of $BF_3 \cdot OEt_2$ (2.85 mL, 23.1 mmol). The mixture was stirred for 4 d at 25 °C, following which triethyl amine (6.1 mL) and CH_2Cl_2 (100 mL) were added, the solution was evaporated under reduced pressure and chromatographed on silica gel using 2:1 hexanes:ethyl acetate as eluent to afford methoxy ketone 44 (214 mg, 50%) as a yellow foam. ^1H NMR (500

MHz, DMSO-d6): δ 8.21 (d, J=7.7 Hz, 1H), 8.16 (d, J=7.8 Hz, 1H), 7.97 (d, J=8.2 Hz, 1H), 7.95 (d, J=8.2 Hz, 1H), 7.88 (d, J=8.6 Hz, 1H), 7.68 (d, J=8.1 Hz, 1H), 7.46 (td, J=1.0, 7.4 Hz, 1H), 7.37 (td, J=1.1, 7.7 Hz, 1H), 7.36 (d, J=7.2 Hz, 1H), 7.30 (app.t, J=7.6 Hz, 1H), 7.23 (app.t, J=7.4 Hz, 1H), 5.02 (s, 1H), 3.94 (dd, J=7.2, 13.7 Hz, 1H), 3.39 (s, 3H), 2.62 (d, J=13.9 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 199.8, 139.4, 135.7, 125.0, 124.8, 124.5, 124.1, 124.0, 120.0, 119.8, 119.4, 119.2, 114.9, 112.1, 111.3, 109.2, 99.0, 88.2, 84.4, 58.9, 45.4, 29.2. IR (thin film/NaCl): 3046.6 (brm), 3003.8 (brw), 2927.9 (m), 2835.6 (m), 1736.6 (s), 1640.5 (m), 1565.8 (m), 1492.7 (m), 1442.9 (s), 1311.5 (s), 1144.3 (m), 1126.1 (s), 740.2 (s) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{25}H_{20}N_2O_3$: 396.1474. Found: 396.1474.

Preparation of desamido TAN-1030a (47) A suspension of ketone 15 (30 mg, 0.08 mmol), hydroxylamine hydrochloride (17 mg, 0.24 mmol), and NaOAc (20 mg, 0.24 mmol) in 50% aqueous EtOH (2.0 mL) was heated gently to reflux for 30 min. Following cooling to room temperature, sovent was removed *in vacuo*, and the residue purified by MPLC (2:1 hexanes:ethyl acetate) to provide oxime 47 (26 mg, 85%) as a yellow powder. ^1H NMR (500 MHz, DMSO-d6): δ 10.43 (s, 1H), 8.17 (d, J=7.8 Hz, 1H), 8.13 (d, J=7.4 Hz, 1H), 7.91 (d, J=8.4 Hz, 1H), 7.89 (d, J=8.4 Hz, 1H), 7.88 (d, J=8.4 Hz, 1H), 7.67 (d, J=8.2 Hz, 1H), 7.44 (app.t, J=7.6 Hz, 1H), 7.34 (app.t, J=7.7 Hz, 1H), 7.27 (app.t, J=7.5 Hz, 1H), 7.20 (app.t, J=7.4 Hz, 1H), 6.98 (d, J=5.5 Hz, 1H), 4.70 (s, 1H), 3.61 (d, J=14.1 Hz, 1H), 3.42 (s, 3H), 2.97 (dd, J=5.7, 14.3 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 145.3, 139.3, 135.9, 126.0, 125.1, 124.9, 124.6, 124.2, 124.0, 120.0, 119.6, 119.4, 119.1, 119.1, 115.0, 111.8, 111.0, 109.1, 95.9, 83.7, 82.2, 58.3, 29.7, 28.4. IR (thin film/NaCl): 3249.5 (brm), 2918.3 (s), 2848.4 (s), 1728.1 (m), 1640.2 (m), 1443.1 (s), 1398.1 (m), 1312.0 (m), 1124.5 (s), 740.7 (s) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{25}H_{21}N_3O_3$: 411.1583. Found: 411.1582.

Preparation of desamido RK-286c (46) To a stirred solution of ketone 15 (12 mg, 0.03 mmol) in 1:1 MeOH: CH_2Cl_2 (1.0 mL) was added $NaBH_4$ (3 mg, 0.08 mmol) at room temperature. After 5 minutes solvent was removed under reduced pressure. To the white residue was added 1 mL 1.0 N HCl on an ice bath. The mixture was stirred for 15 min at 25 °C and extracted with CH_2Cl_2 (3x 1mL). The combined organic phases were dried with Na_2SO_4 and chromatographed on silica gel using 2:1 hexanes:ethyl

acetate as eluent to afford alcohol 46 (12 mg, 95%) as a white solid. ^{1}H NMR (500 MHz, CDCl3): δ 8.14 (d, J=7.7 Hz, 1H), 8.11 (d, J=7.7 Hz, 1H), 7.90 (d, J=8.2 Hz, 1H), 7.85 (d, J=8.2 Hz, 1H), 7.81 (d, J=8.5 Hz, 1H), 7.39 (td, J=1.0, 8.1 Hz, 1H), 7.35 (ddd, J=.14, 7.1, 8.4 Hz, 1H), 7.25 (m, 3H), 6.54 (d, J=5.6 Hz, 1H), 4.34 (m, 1H), 3.66 (d, J=3.0 Hz, 1H), 3.53 (s, 3H), 2.71.dd (3.5, J=14.9 Hz, 1H), 2.45 (m, 1H), 2.30 (s, 3H), 1.66 (bs, 1H). ^{13}C NMR (125 MHz, CDCl3): δ 139.6, 136.6, 128.3, 127.2, 126.5, 126.2, 124.8, 124.4, 123.9, 120.5, 120.3, 119.6, 119.3, 114.9, 112.1, 110.9, 107.6, 90.6, 83.1, 79.7, 60.5, 57.4, 33.7, 29.9. IR (thin film/NaCl): 3528.3 (brm), 3048.1 (m), 3000.2 (m), 2928.4 (m), 1643.7 (m), 1564.8 (m), 1493.8 (m), 1445.1 (s), 1344.4 (m), 1311.6 (s), 1231.2 (s), 1109.5 (brs) cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{25}H_{22}N_2O_3$: 398.1630. Found: 398.1633.

Preparation of aldehyde (+)-50 To a stirred solution of ester (+)-36 (150 mg, 0.243mmol) in THF (2.5 mL) was added $LiBH_4$ (12 mg, 0.535 mmol) at room temperature. After 20 min solvent was removed in vacuo. To the white residue, 10.0 mL 1.0 N HCl was added on an ice bath. The aqueous phase was extracted with CH_2Cl_2 (3x 20 mL). The combined organic phases were dried with Na_2SO_4 and chromatographed on silica gel using 1:1 hexanes:ethyl acetate as eluent to afford a diol (124mg, 89%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d6): δ 9.25 (d, J=7.9 Hz, 1H), 7.97 (d, J=7.2 Hz, 1H), 7.96 (d, J=8.1 Hz, 1H), 7.78 (d, J=8.3 Hz, 1H), 7.48 (app.t, J=7.6 Hz, 1H), 7.43 (app.t, J=7.8 Hz, 1H), 7.29 (app.t, J=7.1 Hz, 1H), 7.28 (app.t, J=7.2 Hz, 1H), 7.02 (s, 1H), 7.96 (dd, J=5.2, 7.2 Hz, 1H), 6.94 (s, 2H), 5.33 (s, 1H), 5.06 (t, J=5.6 Hz, 1H), 5.02 (d, J=17.7 Hz, 1H), 4.95 (d, J=17.6 Hz, 1H), 4.85 (d, J=15.9 Hz, 1H), 4.85 (d, J=15.7 Hz, 1H), 3.85-3.81 (m, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.14 (dd, J=7.6, 13.7 Hz, 1H), 2.15 (s, 3H), 1.94 (dd, J=4.8, 13.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d6): δ 168.9, 148.9, 148.1, 140.0, 136.7, 130.5, 130.2, 128.7, 125.4, 125.3, 124.6, 124.3, 123.8, 122.4, 120.9, 120.0, 119.8, 119.2, 118.5, 115.2, 114.9, 114.0, 112.1, 111.8, 108.7, 100.2, 83.5, 64.7, 55.5, 55.5, 49.6, 45.4, 40.2, 40.1, 21.3. IR (thin film/NaCl): 3343.8 (brm), 3001.5 (w), 2950.7 (m), 2926.1 (m), 1647.4 (s), 1588.0 (m), 1514.4 (m), 1459.7 (s), 1422.2 (m), 1399.6 (m), 1312.4 (m), 1138.0 (s), 744.7 (s) cm^{-1}. $[\alpha]_D^{25}$ +112° (c=0.1, MeOH). To a stirred solution of the diol (395 mg, 0.67 mmol) in 1:1 benzene:DMSO (4.6 mL) was added pyridinium trifluoroacetate (130 mg, 0.67 mmol) followed by 1,3-dicyclohexylcarbodiimide (415 mg, 2.01 mmol). The flask was then quickly

sealed with a septum, evacuated, and flushed with N_2 (3x). The heterogeneous mixture was stirred for 9h until reaction was complete as indicated by TLC. Benzene (5.0 mL) was added to the mixture and the 1,3-dicyclohexylurea (DCU) precipitate was filtered. The filtrate was washed with H_2O (3x 5.0 mL), and the combined aqueous layers were back extracted with CH_2Cl_2 (3x 10.0 mL). All organic layers were combined, dried with Na_2SO_4, and evaporated to an oily residue. A minimum amount of acetone (2 mL) was added to precipitate the remaining DCU. Filtration and evaporation to a yellow oil, which was puified by MPLC (2:1→1:1 hexanes:ethyl acetate) gave aldehyde (+)-50 (280 mg, 71%, 68% 2 steps) as a yellow powder. ^{1}H NMR (500 MHz, DMSO-d6): δ 10.07 (s, 1H), 9.31 (d, J=7.9 Hz, 1H), 8.02 (d, J=8.5 Hz, 1H), 7.99 (d, J=7.7 Hz, 1H), 7.87 (d, J=8.2 Hz, 1H), 7.50 (app.t, J=8.1 Hz, 1H), 7.47 (app.t, J=8.2 Hz, 1H), 7.32 (app.t, J=8.1 Hz, 1H), 7.17 (dd, J=7.2, 4.8 Hz, 1H), 7.04 (s, 1H), 6.94 (d, J=9.6 Hz, 1H), 6.93 (d, J=8.1 Hz, 1H), 6.57 (bs, 1H), 5.02 (d, J=17.6 Hz, 1H), 4.98 (d, J=17.7 Hz, 1H), 4.87 (d, J=15.2 Hz, 1H), 4.83 (d, J=15.2 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.24 (dd, J=7.6, 14.0 Hz, 1H), 2.22 (s, 3H), 2.00 (dd, J=4.5, 14.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d6): δ 202.2, 168.7, 148.9, 148.1, 139.9, 136.9, 130.4, 130.2, 128.2, 125.5, 125.1, 123.9, 123.9, 122.5, 121.1, 120.4, 119.9, 119.6, 119.1, 115.8, 114.6, 114.4, 112.1, 111.8, 109.0, 98.7, 86.8, 84.8, 55.5, 55.5, 49.6, 45.5, 39.4, 22.7. IR (thin film/NaCl): 3253.9 (brm), 3010.7 (m), 2953.6 (m), 2934.0 (m), 2833.9 (s), 1734.0 (s), 1646.2 (s), 1614.7 (w), 1589.9 (m), 1514.1 (m), 1399.1 (s), 1275.7 (m), 1138.4 (s), 1024.8 (m), 745.1 (s) cm^{-1}. $[\alpha]_D^{25}$ +48° (c=0.1, MeOH).

Preparation of hydroxy ketone (+)-51 To a suspension of aldehyde (+)-50 (100 mg, 0.170 mmol) in Et_2O (17.0 mL) was added $BF_3 \cdot OEt_2$ (23 μL, 0.187 mmol) and the mixture stirred vigorously for 12h at 25-30 °C, when again was treated with $BF_3 \cdot OEt_2$ (23 μL, 0.187 mmol) and stirred for an additional 12 h at the same temperature. The reaction mixture was filtered to provide ketone (+)-51 (85 mg, 85%) as a white powder. ^{1}H NMR (500 MHz, DMSO-d6, 310 K): δ 9.35 (d, J=7.9 Hz, 1H), 8.06 (d, J=8.6 Hz, 1H), 7.92 (d, J=7.7 Hz, 1H), 7.72 (d, J=8.2 Hz, 1H), 7.53 (app.t, J=7.6 Hz, 1H), 7.43 (app.t, J=8.1 Hz, 1H), 7.40 (d, J=6.6 Hz, 1H), 7.35 (app.t, J=7.5 Hz, 1H), 7.29 (app.t, J=7.4 Hz, 1H), 7.02 (s, 1H), 6.93 (s, 2H), 6.12 (d, J=5.1 Hz, 1H), 5.23 (d, J=4.5 Hz, 1H), 4.96 (s, 2H), 4.85 (d, J=15.1 Hz, 1H), 4.81 (d, J=15.1 Hz, 1H), 3.97 (dd, J=6.7, 14.1 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H),

2.66 (d, J=14.1 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (500 MHz, DMSO-d6): δ 201.1, 168.6, 148.9, 148.1, 140.3, 136.0, 130.4, 129.8, 126.9, 125.6, 125.5, 124.9, 124.0, 123.6, 122.8, 120.7, 120.4, 119.9, 119.9, 118.8, 115.9, 115.1, 114.3, 112.1, 111.8, 109.2, 100.5, 84.4, 80.0, 55.5, 55.5, 49.6, 45.4, 44.9, 29.4. IR (thin film/NaCl): 3300.0 (brs), 2999.5 (brm), 2848.6 (m), 1728.9 (m), 1665.5 (s), 1503.3 (m), 1451.2 (s), 1406.8 (m), 1132.8 (s), 1021.9 (m), 750.6 (s) cm^{-1}. $[\alpha]_D^{25}$ +83° (c=0.1, DMSO).

Preparation of Ester (+)-35 To a solution of ketone (+)-51 (10 mg, 0.017 mmol) in 1:1 MeOH/CH_2Cl_2 (1.0 mL) was added Copper (I) chloride (30 mg, 0.30 mmol), and the mixture warmed to reflux for 15 min. Solvent was removed *in vacuo* and the resulting residue subjected to silica gel chromatography (1:1, hexanes:ethyl acetate) to afford (+)-36 (10 mg, 95%) as a colorless solid.

Preparation of diol (+)-53 To a stirred solution of ketone (+)-51 (85 mg, 0.15 mmol) in 1:1:2 MeOH:CH_2Cl_2:$CHCl_3$ (20.0 mL), $NaBH_4$ (20 mg, 0.53 mmol) was added at room temperature. After 5 minutes solvent was removed under reduced pressure. To the white residue, 10 mL 1.0 N HCl was added on an ice bath. The mixture was stirred for 15 min at 25 °C and extracted with CH_2Cl_2 (3x 20 mL). The combined organic phases were dried with Na_2SO_4 and chromatographed on silica gel using 1:1 hexanes:ethyl acetate as eluent to afford alcohol (+)-53 (81 mg, 95%) as a white solid. ^1H NMR (500 MHz, acetone-d6): δ 9.53 (d, J=7.9 Hz, 1H), 8.11 (d, J=8.5 Hz, 1H), 7.88 (d, J=7.7 Hz, 1H), 7.51 (d, J=8.2 Hz, 1H), 7.46 (app.t, J=7.2 Hz, 1H), 7.36 (app.t, J=7.9 Hz, 1H), 7.29 (app.t, J=7.4 Hz, 1H), 7.22 (app.t, J=7.4 Hz, 1H), 7.08 (s, 1H), 6.98 (d, J=8.3 Hz, 1H), 6.91 (d, J=8.2 Hz, 1H), 6.76 (d, J=5.1 Hz, 1H), 4.95 (d, J=17.1 Hz, 1H), 4.90 (d, J=71.1 Hz, 1H), 4.89 (d, J=15.2 Hz, 1H), 4.85 (d, J=15.2 Hz, 1H), 4.24 (d, J=.85 Hz, 1H), 4.23 (bs, 1H), 4.14 (d, J=8.6 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.64 (bs, 1H), 2.76 (d, J=15.1 Hz, 1H), 2.65 (d, J=15.1 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, acetone-d6): δ 170.4, 150.6, 149.7, 141.2, 137.7, 132.0, 130.7, 130.4, 127.6, 127.1, 125.8, 125.3, 125.0, 124.3, 121.5, 121.0, 120.6, 120.0, 119.8, 116.6, 116.0, 115.0, 112.8, 108.9, 93.3, 80.6, 74.7, 65.4, 56.1, 50.4, 46.6, 35.4, 30.4. IR (thin film/NaCl): 3355.5 (brm), 2922.9 (m), 2847.8 (m), 1654.5 (s), 1501.5 (w), 1449.3 (s), 1254.5 (s), 1136.8 (s), 1025.7 (m), 747.1 (s) cm^{-1}. $[\alpha]_D^{25}$ +37° (c=0.1, MeOH).

Preparation of methyl ether (+)-54 To a stirred suspension of NaH (14 mg, 0.58 mmol) in THF (1.0 mL) was added a solution of alcohol (+)-53 (81 mg, 0.138 mmol) in THF (7 mL). The resulting mixture was stirred for 10 min with the visible evolution of gas, and for an additional 15 min thereafter. Addition of MeI (9.5 μL, 0.15 mmol) produced a single product by TLC (2.5:1 hexanes:acetone). After approximately 50 min the reaction was quenched by addition of 1.0 mL 1.0N HCl followed by 2.0 mL H_2O. Extraction of the solution with CH_2Cl_2 (3x 10 mL), drying over Na_2SO_4 and evaporation to a residue which could be purified by MPLC (2.5:1 hexanes:acetone) provided methyl ether (+)-54 (67 mg, 80%) as a yellow foam. ^1H NMR (500 MHz, $CDCl_3$): δ 9.54 (d, J=7.9 Hz, 1H), 7.90 (d, J=8.5 Hz, 1H), 7.81 (d, J=7.7 Hz, 1H), 7.48 (app.t, J=7.6 Hz, 1H), 7.41 (app.t, J=7.2 Hz, 1H), 7.38 (app.t, J=7.2 Hz, 1H), 7.28 (m, 2H), 6.97 (d, J=8.2 Hz, 1H), 6.95 (s, 1H), 6.86 (d, J=8.1 Hz, 1H), 6.60 (d, J=5.8 Hz, 1H), 4.96 (d, J=15.0 Hz, 1H), 4.89 (d, J=15.0 Hz, 1H), 4.84 (d, J=16.7 Hz, 1H), 4.79 (d, J=16.6 Hz, 1H), 4.38 (d, J=2.6 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.71 (d, J=2.6 Hz, 1H), 3.57 (s, 3H), 2.76 (dd, J=3.1, 15.1 Hz, 1H), 2.50 (bd, J=14.7 Hz, 1H), 2.3 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 315 K): δ 170.3, 149.6, 148.7, 140.1, 136.8, 130.8, 129.4, 127.0, 126.4, 125.3, 124.8, 124.3, 123.7, 120.7, 120.4, 120.2, 120.0, 119.6, 116.0, 115.5, 114.5, 111.6, 111.5, 107.1, 90.7, 83.2, 79.5, 60.6, 57.4, 56.1, 56.0, 49.9, 46.5, 33.6, 30.1. IR (thin film/NaCl): 3423.7 (brm), 2923.2 (s), 2848.1 (m), 2636.2 (m), 1647.2 (s), 1514.3 (m), 1462.9 (s), 1258.0 (m), 1235.3 (m), 1136.9 (m), 1026.9 (w), 743.3 (s) cm^{-1}. $[\alpha]_D^{25}$ +48° (c=0.1, MeOH).

Preparation of (+)-RK-286c (50) To a stirred solution of ether (+)-54 (10 mg, 0.017 mmol) in anisole or thioanisole (80 μL, ≈50 equiv) was added TFA (0.5 mL). The reaction was monitored by TLC, and after 24 h had proceeded to completion, whereupon 1.0 mL H_2O was added, followed by extraction with CH_2Cl_2 (3x 5mL). Combined organic layers were washed with saturated aqueous $NaHCO_3$ (5 mL), dried over Na_2SO_4, and evaporated to a residue, which was purified by preparative TLC (5% MeOH:CH_2Cl_2) to provide (+)-RK-286c (50, 6 mg, 75%). ^1H NMR (500 MHz, DMSO-d_6): δ 9.27 (d, J=7.9 Hz, 1H), 8.47 (bs, 1H), 7.99 (d, J=8.5 Hz, 1H), 7.94 (d, J=7.7 Hz, 1H), 7.59 (d, J=8.2 Hz, 1H), 7.45 (app.t, J=7.4 Hz, 1H), 7.40 (app.t, J=7.5 Hz, 1H), 7.26 (app.t, J=7.5 Hz, 1H), 6.78 (d, J=5.3

Hz, 1H), 4.95 (d, J=17.6 Hz, 1H), 4.89 (d, J=17.7 Hz, 1H), 4.25 (bs, 1H), 4.17 (bs, 1H), 3.83 (d, J=2.7 Hz, 1H), 3.41 (s, 3H), 2.60 (ddd, J=3.2, 5.6, 14.8 Hz, 1H), 2.41 (dd, J=3.3, 14.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 139.7, 136.1, 129.5, 125.5, 124.7, 124.1, 123.9, 122.6, 120.6, 119.5, 118.9, 118.6, 115.7, 108.6, 90.9, 82.3, 79.5, 58.8, 56.4, 45.3, 33.9, 29.9. IR (thin film/NaCl): 3354.0 (brm), 2920.4 (s), 2851.6 (m), 1677.2 (s), 1636.0 (m), 1585.3 (m), 1456.2 (s), 1352.8 (s), 1318.7 (s), 1231.7 (m), 1117.3 (m), 743.8 (s) cm^{-1}. $[\alpha]_D^{25}$ +41.1° (c=0.18, EtOAc); natural RK-286c $[\alpha]_D^{20}$ +45.3° (c=0.22, EtOAc).

Preparation of Diol (+)-55 To a stirred solution of ether (+)-54 (112 mg, 0.186 mmol) in $CDCl_3$ (2.0 mL) was added Martin's sulfurane (187 mg, 0.28 mmol). The reaction rapidly proceeded to a less polar product as monitored by TLC, and after 20 min was complete. Solvent was evaporated and the reidue subjected to silica gel chromatography (2:1 hexanes:ethyl acetate) to provide an olefin (96 mg, 88%) as a white solid. ^1H NMR (500 MHz, DMSO-d6, 315 K): δ 9.31 (d, J=7.9 Hz, 1H), 8.11 (d, J=8.6 Hz, 1H), 7.91 (d, J=7.7 Hz, 1H), 7.86 (d, J=8.2 Hz, 1H), 7.50 (td, J=1.0, 7.34 Hz, 1H), 7.43 (app.t, J=7.8 Hz, 1H), 7.31 (app.t, J=7.0 Hz, 1H), 7.28 (app.t, J=7.1 Hz, 1H), 7.13 (d, J=1.9 Hz, 1H), 7.02 (s, 1H), 6.93 (d, J=8.6 Hz, 1H), 6.92 (d, J=8.6 Hz, 1H), 6.09 (d, J=10.4 Hz, 1H), 5.77 (dt, J=2.3, 10.4 Hz, 1H), 4.95 (s, 2H), 4.85 (d, J=15.1 Hz, 1H), 4.81 (d, J=15.1 Hz, 1H), 4.48 (d, J=1.4 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.57 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, acetone-d6): δ 169.9, 150.5, 149.7, 141.3, 137.4, 131.8, 131.2, 130.5, 127.7, 127.1, 126.4, 126.2, 125.5, 125.3, 124.3, 121.5, 121.2, 121.1, 120.5, 120.4, 118.0, 117.1, 115.9, 112.8, 112.8, 109.1, 91.5, 80.8, 78.8, 57.7, 56.0, 56.0, 50.5, 46.5, 28.0. IR (thin film/NaCl): 2920.5 (s), 2851.5 (s), 1709.8 (m), 1674.3 (s), 1589.0 (m), 1513.7 (m), 1457.5 (s), 1222.9 (m), 1026.6 (m), 745.3 (m) cm^{-1}. $[\alpha]_D^{25}$ +36° (c=0.1, MeOH). To a stirred solution of 4-methylmorpholine N-oxide (6 mg, 0.05 mmol) and OsO_4 (0.6 mL of a 2.5% solution in *t*-BuOH, 0.05 mmol) in 4:1 acetone:H_2O (2 mL) was added solution of the olefin (25 mg, 0.043 mmol) in acetone (1 mL). The reaction was monitored by TLC, and after 16 h had proceeded to completion, whereupon 100 mg $NaHSO_3$ was added in 1.0 mL H_2O, and the black solution was stirred for 20 min and filtered, followed by extraction with CH_2Cl_2 (3x 15mL). Combined organic layers were dried over Na_2SO_4, and evaporated to a residue, which was purified by MPLC (1:1 hexanes:ethyl

acetate) to provide diol (+)-55 (23 mg, 84%) as a white powder. ^{1}H NMR (500 MHz, DMSO-d6): δ 9.86 (d, J=7.9 Hz, 1H), 7.95 (d, J=8.6 Hz, 1H), 7.94 (d, J=7.6 Hz, 1H), 7.64 (d, J=8.1 Hz, 1H), 7.55 (app.t, J=7.6 Hz, 1H), 7.45 (app.t, J=7.7 Hz, 1H), 7.35 (app.t, J=7.5 Hz, 1H), 7.29 (app.t, J=7.5 Hz, 1H), 7.02 (s, 1H), 6.94 (s, 2H), 6.59 (d, J=1.6 Hz, 1H), 6.18 (d, J=3.8 Hz, 1H), 5.07 (d, J=6.0 Hz, 1H), 4.99 (d, J=17.8 Hz, 1H), 4.95 (d, J=17.8 Hz, 1H), 4.83 (s, 2H), 4.12 (d, J=10.1 Hz, 1H), 4.12 (dd, J=2.3, 3.8 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.55 (ddd, J=2.3, 6.1, 10.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 168.8, 148.9, 148.1, 140.3, 136.5, 130.4, 129.9, 127.8, 125.7, 125.0, 124.7, 123.5, 122.7, 120.8, 120.2, 119.9, 119.9, 118.7, 115.5, 114.8, 114.1, 112.0, 111.7, 108.8, 95.6, 87.3, 83.1, 71.7, 65.6, 61.6, 55.5, 55.5, 49.6, 45.5, 29.0. IR (thin film/NaCl): 3411.2 (brm), 2929.3 (m), 2849.4 (w), 2656.3 (m), 1590.0 (m), 1514.0 (m), 1461.2 (s), 1350.9 (m), 1273.6 (s), 1127.1 (s), 1025.0 (m), 743.3 (s) cm^{-1}. $[\alpha]_D^{25}$ +17° (c=0.1, MeOH).

Preparation of (+)-MLR-52 (51) To a stirred solution of diol (+)-55 (10 mg, 0.016 mmol) in anisole or thioanisole (80 μL, ≈50 equiv) was added TFA (0.5 mL). The reaction was monitored by TLC, and after 16 h had proceeded to completion, whereupon 1.0 mL H_2O was added, followed by extraction with CH_2Cl_2 (3x 5mL). Combined organic layers were washed with saturated aqueous $NaHCO_3$ (5 mL), dried over Na_2SO_4, and evaporated to a residue, which was purified by preparative TLC (5% MeOH:CH_2Cl_2) to provide (+)-MLR-52 (51, 6 mg, 77%). ^{1}H NMR (500 MHz, DMSO-d6): δ 9.31 (d, J=7.9 Hz, 1H), 8.61 (bs, 1H), 7.99 (d, J=7.7 Hz, 1H), 7.96 (d, J=8.7 Hz, 1H), 7.62 (d, J=8.2 Hz, 1H), 7.53 (app.t, J=7.5 Hz, 1H), 7.45 (td, J=0.8, 7.7 Hz, 1H), 7.32 (app.t, J=7.4 Hz, 1H), 7.32 (app.t, J=7.4 Hz, 1H), 6.58 (d, J=1.6 Hz, 1H), 6.12 (d, J=4.0 Hz, 1H), 5.06 (d, J=5.9 Hz, 1H), 4.99 (d, J=17.6 Hz, 1H), 4.95 (d, J=17.5 Hz, 1H), 4.13 (d, J=10.3 Hz, 1H), 4.12 (dd, J=1.6, 2.6 Hz, 1H), 3.62 (s, 3H), 3.56 (ddd, J=2.6, 6.2, 10.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d6): δ 171.8, 140.2, 136.4, 132.6, 127.8, 125.8, 125.5, 124.8, 124.6, 123.6, 122.7, 120.9, 120.1, 119.7, 119.3, 115.4, 114.9, 114.3, 108.7, 95.6, 87.2, 83.1, 71.7, 65.6, 61.6, 45.4, 29.0. IR (thin film/NaCl): 3348.5 (brm), 2922.9 (s), 2851.9 (m), 1638.2 (s), 1586.6 (m), 1455.5 (s), 1373.5 (m), 1336.6 (m), 1320.8 (m), 1275.0 (m), 1224.7 (m), 1200.3 (w), 1119.5 (s), 740.8 (s,) cm^{-1}. $[\alpha]_D^{25}$ +65° (c=0.1, MeOH); natural MLR-52 $[\alpha]_D$ +68° (c=0.093, MeOH).

Preparation of oxime (-)-56 A suspension of ketone (+)-51 (100 mg, 0.17 mmol), hydroxylamine hydrochloride (165 mg, 2.38 mmol), and NaOAc (167 mg, 2.04 mmol) in 80% aqueous EtOH (35.0 mL) was heated gently to reflux for 30 min. Following cooling to room temperature, sovent was removed *in vacuo*, and the residue purified by MPLC (1:1 hexanes:ethyl acetate) to provide oxime (-)-56 (98 mg, 95%) as a yellow powder. ^{1}H NMR (500 MHz, DMSO-d6): δ 10.3 (s, 1H), 9.34 (d, J=7.9 Hz, 1H), 8.08 (d, J=8.6 Hz, 1H), 7.90 (d, J=7.6 Hz, 1H), 7.71 (d, J=8.3 Hz, 1H), 7.51 (app.t, J=7.6 Hz, 1H), 7.42 (app.t, J=7.9 Hz, 1H), 7.32 (app.t, J=7.7 Hz, 1H), 7.28 (app.t, J=7.4 Hz, 1H), 7.04 (d, J=6.8 Hz, 1H), 7.03 (s, 1H), 6.95 (d, J=8.4 Hz, 1H), 6.93 (d, J=8.2 Hz, 1H), 5.56 (m, 2H), 4.97 (d, J=18.1 Hz, 1H), 4.93 (d, J=16.9 Hz, 1H), 4.85 (d, J=15.0 Hz, 1H), 4.45 (d, J=15.0 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.61 (d, J=13.9 Hz, 1H), 3.01 (dd, J=5.8, 14.3 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 168.8, 148.9, 148.1, 147.4, 140.2, 136.1, 130.5, 129.6, 128.1, 125.4, 125.3, 124.7, 124.6, 123.6, 122.8, 120.5, 120.1, 119.9, 119.6, 118.5, 116.0, 114.8, 113.9, 112.1, 111.9, 108.9, 97.4, 82.0, 74.9, 55.5, 55.5, 49.5, 45.5, 29.6, 28.6. IR (thin film/NaCl): 3324.0 (brm), 2995.0 (w), 2911.3 (m), 1660.0 (s), 1589.7 (m), 1513.5 (s), 1461.1 (s), 1417.9 (m), 1399.0 (m), 1349.2 (s), 1315.5 (m), 1260.0 (s), 1234.6 (m), 1124.4 (m), 1027.2 (m), 741.7 (s) cm^{-1}. $[\alpha]_D^{20}$ -18° (c=0.1, CH_2Cl_2).

Preparation of methoxy oxime (-)-57 To a mixture of oxime (-)-56 (90 mg, 0.15 mmol), MeI (88μL, 1.42 mmol), and powdered KOH (88 mg, 1.58 mmol) was added *n*-Bu4NBr (10 mg, 0.03 mmol). The mixture was stirred under N_2 for 30 min, solvent was removed *in vacuo*, and the residue was subjected to silica gel chromatography (1:1 hexanes:ethyl acetate) to provide methoxime (-)-57 (85 mg, 90%) as a yellow powder. ^{1}H NMR (500 MHz, DMSO-d6, 345 K): δ 9.36 (d, J=8.0 Hz, 1H), 7.99 (d, J=8.6 Hz, 1H), 7.93 (d, J=7.8 Hz, 1H), 7.68 (d, J=8.3 Hz, 1H), 7.51 (app.t, J=7.6 Hz, 1H), 7.44 (app.t, J=7.8 Hz, 1H), 7.33 (app.t, J=7.2 Hz, 1H), 7.30 (app.t, J=7.1 Hz, 1H), 7.04 (s, 1H), 7.02 (d, J=5.6 Hz, 1H), 6.97 (d, J=9.4 Hz, 1H), 6.94 (d, J=8.1 Hz, 1H), 4.97 (s, 2H), 4.86 (d, J=15.5 Hz, 1H), 4.85 (d, J=15.7 Hz, 1H), 4.76 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (d, J=14.4 Hz, 1H), 3.45 (s, 3H), 3.16 (dd, J=5.9, 14.4 Hz, 1H), 3.14 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6): δ 168.7, 148.9, 148.1, 147.3, 139.8, 136.1, 130.4,

129.5, 128.0, 125.4, 125.3, 124.7, 124.6, 123.6, 122.7, 120.6, 120.2, 119.9, 119.6, 118.6, 115.5, 114.9, 113.8, 112.2, 112.0, 108.9, 96.1, 83.3, 82.0, 60.8, 58.4, 55.5, 55.5, 49.5, 45.4, 30.4, 28.5. IR (thin film/NaCl): 2998.0 (w), 2926.3 (m), 1674.1 (s), 1590.0 (m), 1513.7 (s), 1460.9 (s), 1418.2 (m), 1397.9 (s), 1349.4 (s), 1316.2 (s), 1262.1 (m), 1225.6 (m), 1044.3 (m), 743.5 (m) cm^{-1}. $[\alpha]_D^{25}$ -22° (c=0.1, CH_2Cl_2).

Preparation of amine (+)-58 A mixture of oxime (+)-57 (85 mg, 0.13 mmol) and PtO_2 (28 mg) in a 60% aqueous acetic acid (15.0 mL) was treated with H_2, and the reaction was monitored by TLC (1:1 hexanes:ethyl acetate). Upon completion, the mixture was filtered through celite and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (40 mL) and washed with 8.0 mL 1.0N NaOH. The aqueous layer was then back-extracted with CH_2Cl_2 (2x 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to a residue (79 mg), which was used in the next step without further purification. An analitical sample of primary amine (+)-58 could be obtained by preparative TLC of the above residue using 5% MeOH:CH_2Cl_2 as eluent. ^1H NMR (500 MHz, $CDCl_3$, 310 K): δ 9.55 (d, J=7.9 Hz, 1H), 7.95 (d, J=8.5 Hz, 1H), 7.83 (d, J=7.7 Hz, 1H), 7.51 (app.t, J=7.6 Hz, 1H), 7.42 (app.t, J=8.2 Hz, 1H), 7.40 (app.t, J=7.5 Hz, 1H), 7.30 (app.t, J=7.8 Hz, 2H), 6.99 (d, J=9.4 Hz, 2H), 6.87 (d, J=8.0 Hz, 1H), 6.59 (d, J=4.9 Hz, 1H), 4.98 (d, J=14.9 Hz, 1H), 4.92 (d, J=14.9 Hz, 1H), 4.87 (d, J=16.7 Hz, 1H), 4.82 (d, J=16.7 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.75 (m, 2H), 3.46 (s, 3H), 2.63 (m, 2H), 2.32 (s, 3H), 1.27 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 315 K): δ 170.2, 149.6, 148.7, 140.1, 137.0, 130.8, 129.6, 129.5, 127.0, 126.2, 125.4, 124.7, 124.5, 123.8, 120.8, 120.5, 120.2, 120.2, 119.6, 116.0, 115.4, 114.6, 111.6, 111.6, 107.4, 91.3, 84.2, 80.2, 57.5, 56.1, 56.1, 49.9, 46.5, 42.6, 34.6, 30.0. IR (thin film/NaCl): 3414.7 (brw), 2920.8 (s), 2851.7 (s), 1733.7 (w), 1672.8 (s), 1636.0 (w), 1588.1 (m), 1513.5 (s), 1352.7 (s), 1259.3 (s), 1136.7 (m), 744.2 (m) cm^{-1}. $[\alpha]_D^{25}$ +14.3° (c=0.14, $CHCl_3$).

Preparation of (+)-staurosporine (49) Crude amine (+)-58 was dissolved in THF (2.0 mL) and treated with formic acetic anhydride in THF (1.3 μL of a 1.3 M solution in THF, 0.17 mmol)(FAA prepared by treatment of 1.0 equiv acetic anhydride with 1.2 equiv formic acid followed by reflux for 2 h). TLC analysis showed rapid formation of a less polar substance. A stream of N_2

was used to evaporate the solvent, followed by high vacuum for 15 min. THF (1.3 mL) was added to dissolve the residue, the reaction vessel was cooled to 0 °C, and BH_3•DMS (193 μL of a 2.0 N solution in toluene, 0.39 mmol) was introduced. The solution was heated to reflux for 2 h at which point it was again cooled to 0 °C. Methanolic HCl (1.0 mL) was added along with excess MeOH (1.3 mL) and the solution was refluxed for an additional hour. Following cooling, volitiles were removed *in vacuo*, and the solid residue was azeotroped with MeOH (5x 5.0 mL). To the remaining residue was added 7.0 mL CH_2Cl_2 followed by 1.0 N NaOH (5.0 mL), layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3x 7.0 mL). Combined organic layers were dried over Na_2SO_4, evaporated, and purified by MPLC (5% MeOH:CH_2Cl_2) to give a methyl amine (80 mg, 91% 2 steps from 14) as a yellow foam. ^1H NMR (500 MHz, $CDCl_3$, 320 °K): δ 9.55 (d, J=7.9 Hz, 1H), 7.89 (d, J=8.5 Hz, 1H), 7.82 (d, J=7.3 Hz, 1H), 7.48 (td, J=1.0, 7.5 Hz, 1H), 7.39 (td, J=1.0, 7.4 Hz, 1H), 7.38 (app.t, J=7.3 Hz, 1H), 7.27 (m, 2H), 7.01 (m, 2H), 6.88 (d, J=8.7 Hz, 1H), 6.57 (dd, J=1.4, 6.0 Hz, 1H), 4.98 (d, J=14.9 Hz, 1H), 4.91 (d, J=14.9 Hz, 1H), 4.84 (s, 2H), 3.92 (d, J=3.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.37 (dd, J=3.8, 7.7 Hz, 1H), 3.33 (bs, 3H), 2.72 (ddd, J=1.3, 4.6, 14.5 Hz, 1H), 2.46 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 149.3, 148.4, 139.6, 136.7, 130.6, 130.4, 129.3, 127.1, 126.6, 125.1, 124.5, 124.3, 123.5, 120.7, 120.4, 120.0, 119.8, 119.1, 115.5, 114.9, 114.0, 111.2, 111.2, 107.0, 91.2, 83.9, 80.2, 57.5, 56.0, 55.9, 50.7, 49.9, 46.4, 33.2, 30.1, 29.9. IR (thin film/NaCl): 2954.1 (m), 2915.1 (m), 1673.2 (s), 1635.8 (m), 1462.7 (s), 1399.0 (s), 1352.6 (s), 1258.7 (m), 1136.5 (m), 1026.9 (m), 745.2 (s) cm^{-1}. $[\alpha]_D^{25}$ +22° (c=0.1, MeOH).

To a stirred solution of the amine (10 mg, 0.016 mmol) in anisole or thioanisole (80 μL, ≈50 equiv) was added TFA (0.5 mL). The sluggish reaction was monitored by TLC, and after 48 h had proceeded to completion, whereupon 1.0 mL H_2O was added, and the solution was adjusted to pH10 with 5.0 N NaOH, followed by extraction with CH_2Cl_2 (3x 5mL). Combined organic layers were dried over Na_2SO_4, and evaporated to a residue, which was purified by preparative TLC (5% MeOH:CH_2Cl_2) to provide (+)-Staurosporine (49, 6 mg, 70%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.43 (d, J=7.9 Hz, 1H), 7.94 (8.5, 1H), 7.90 (d, J=7.7 Hz, 1H), 7.49 (app.t, J=7.6 Hz, 1H), 7.43 (app.t, J=7.7 Hz, 1H), 7.37 (app.t, J=7.5 Hz, 1H), 7.33 (app.t, J=7.4 Hz, 1H), 7.30 (d, J=8.0 Hz, 1H), 6.57 (d, J=5.6 Hz, 1H), 6.33 (bs, 1H), 5.05 (d, J=15.8 Hz, 1H), 5.01 (d, J=15.8 Hz, 1H), 3.89 (bs, 1H),

3.42 (s, 3H), 3.37 (d, 8.2H), 2.76 (dd, J=3.9, 14.7 Hz, 1H), 2.41 (bd, J=15.4 Hz, 1H), 2.37 (s, 3H), 1.59 (bs, 1H), 1.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 139.8, 136.7, 132.2, 130.8, 126.6, 125.0, 124.6, 124.2, 123.4, 120.6, 120.0, 119.8, 115.3, 114.1, 106.9, 91.1, 84.2, 80.1, 57.2, 50.4, 45.9, 33.3, 30.3, 30.1. IR (thin film/NaCl): 3316.6 (m), 2925.0 (m), 2850.8 (m), 1678.7 (s), 1636.2 (m), 1584.2 (m), 1457.5 (s), 1352.2 (s), 1316.7 (s), 1281.3 (m), 1115.5 (m), 744.8 (s) cm^{-1}. $[\alpha]_D^{25}$ +35° (c=0.1, MeOH); natural staurosporine $[\alpha]_D^{25}$ +35° (c=1.0, MeOH).